Corrosion of Copper in Acid-Sulfate Plating Baths

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Equilibrium between acid-sulfate plating baths and copper metal places two restrictions on the electrochemical potentials of Cu(I) and Cu(II).

$$\mu_{Cu(I)} = \mu_{Cu(II)} + \mu_e \qquad [1]$$

$$\mu_{Cu(I)} = \mu_{Cu} - \mu_e \qquad [2]$$

For fixed Cu and Cu(II) activity, these constraints determine the electrode potential and activity of Cu(I). For a typical plating bath, the equilibrium concentration of Cu(I) is of the order of one millimolar.

In solution that has been exposed to air, the Cu(I) concentration is reduced by reaction with oxygen. When the solution is subsequently brought into contact with copper metal, Cu(II) reacts with the metal to produce Cu(I) and restore equilibrium. This reaction can be regarded as a corrosion couple made up of the half-cell reactions,

Reaction 1 $\qquad Cu \Rightarrow Cu^{1+} + e^- \qquad$ [3]

Reaction 2 $\qquad Cu^{2+} + e^- \Rightarrow Cu^{1+} \qquad$ [4]
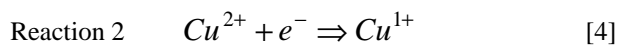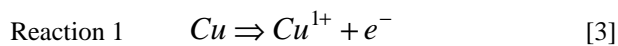
Reaction 1 is in interfacial equilibrium and its rate is limited by diffusion of Cu(I) from the surface. If dissolved oxygen is present in the bulk solution, reaction 1 is sustained by consumption of Cu(I) at a reaction plane within the mass-transfer boundary layer, and the corrosion rate is higher than in deaerated solution. Reaction 2 is kinetically limited because of the high concentration of Cu(II) and the relatively slow kinetics of this elementary step. As a result, the corrosion potential is negative of the equilibrium potential, and this negative shift produces behavior that is different from a typical oxygen reduction-metal dissolution couple. For instance, in a differential aeration cell under this mechanism, metal dissolves in the oxygen-rich region, rather than the oxygen-poor region. Conditions may even exist under which metal is deposited in the oxygen poor region.

We have previously presented a model of this corrosion couple for copper sulfate/sulfuric acid solutions based on diffusion alone. In this report, we present computational results for a more complete model that includes migration as well as chloride. This model incorporates some features of the reaction plane model of Georgidou et al, but takes a different approach to complexation of Cu(I) by chloride. The model is used to evaluate the influences of dissolved oxygen and chloride concentration on dissolution rate and its dependence on boundary layer thickness. The computational results are compared with measured corrosion potentials and RRDE measurements of Cu(I) flux. We also show how these results bear on the distribution of corrosion over features such as trenches.